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⑩ **CANADIAN PATENT**

⑤4 **PHOSGENATION OF AMINES**

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U. S. A.

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PHOSGENATION OF AMINES

This invention relates to a method of phosgenating amines and more particularly to a method of rapidly and intimately mixing phosgene with organic amines to prepare an organic isocyanate.

It has been proposed heretofore to prepare organic isocyanates by reacting organic amines with phosgene in high speed mixers. It is customary in this reaction to have an initial product which is an amine hydrochloride recirculated through a high speed mixer to provide for intimate mixing between the amine and phosgene. Such a process is proposed for example in U.S. Patent 3,188,337. Even where the organic amine and phosgene are mixed under turbulent flow in a closed chamber as proposed in this patent, the time required for initial contact between all of the amine and the excess phosgene is long enough that considerable by-products result. Thus, when one mixes an organic amine with phosgene, a variety of products are possible. This accounts for the fact that heretofore there have been proposed a variety of methods for preparing organic isocyanates, some of which are carried out in the vapor phase and some in the liquid phase. The vapor phase reaction is limited primarily to monoisocyanates containing 5 to 12 carbon atoms. The higher boiling isocyanates usually give poorer yields when prepared by phosgenation of the corresponding amine in the vapor phase than when prepared by a liquid phase process. In any phosgenation, whether in the liquid phase or vapor phase, there are numerous side reactions. The side reactions are possible because of the failure of all of the amine to be contacted by the excess phosgene as rapidly as it need be in order to prevent the side reactions.

In the heretofore known type of high speed mixers, localized high concentrations of organic amine result in the reaction of two mols of amine with one mol of phosgene to produce undesirable urea containing by-products.

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These are carried through the reaction without conversion to isocyanates and end up as tarry by-products which at best must be separated and reacted with water in order to regenerate the starting amine. Often they become so polymerized in the distillation procedure for separating the isocyanate from the by-product that they cannot be regenerated even with high pressure steam and high levels of caustic.

It has also become important to prepare mixtures of organic polyisocyanates by phosgenating the reaction product of aniline with formaldehyde. Aniline reacts with formaldehyde to prepare mixtures of diamines with triamines and higher polyamines. This mixture can be desirably phosgenated to prepare so-called unrefined isocyanates. Often, however, when the heretofore known high speed mixers are used to carry out the phosgenation of the mixture of amines, the amount of by-products is undesirably high. This again results from the formation of urea by-products and other by-products in the phosgenation of the amine due to inadequate mixing. Since these products cannot be distilled, the by-product ureas etc. are not readily separated when they separate as solids, which are frequently very finely divided and troublesome to remove.

It is therefore an object of this invention to provide an improved process for the phosgenation of organic amines. Another object of this invention is to provide for the instantaneous and complete mixing of phosgene with organic amines without localized high concentration of amine. Still a further object of this invention is to provide a process for the phosgenation of amines which prepares high grade organic isocyanates. A still further object of this invention is to provide a continuous process for rapidly and efficiently phosgenating an organic amine. Still a further object of this invention is to provide a method of phosgenating organic amines to prepare organic isocyanates in improved yields. A further object of this invention is to pro-

vide an improved process for the high speed phosgenation of an organic amine.

The foregoing objects and others which will become apparent from the following description are accomplished, generally speaking, by providing a process for the phosgenation of an organic amine which comprises passing  
5 phosgene through an acoustic generator to create a resonance zone having a frequency of from about 10,000 cycles per second to about 30,000 cycles per second, injecting liquid amine into said resonance zone and collecting the resulting isocyanates. Thus, this invention contemplates an improved process for the high speed mixing of phosgene with an organic amine wherein a zone of  
10 resonance having a frequency of from about 10,000 cycles per second to about 30,000 cycles per second is created by passing phosgene through an acoustic generator and then a liquid amine, perhaps in an inert solvent therefor, is injected into this zone of resonance created by the phosgene so that the two reactants are instantly reacted. The product is present as a mist mixed  
15 with gaseous phosgene and by-product HCl. This can desirably be separated from the product by passing the mist to a cyclone separator so that the liquid droplets are condensed and removed from the bottom of the separator and the by-product, hydrogen chloride, removed from the top of the separator as a gas. If desired, the gaseous phosgene and HCl can be separated by condens-  
20 ing the mixture and separating the HCl as a gas. From an economical point of view, it is desirable to again vaporize phosgene and recycle it through the acoustic device.

The foregoing objects and others will also become apparent from the accompanying drawing in which like reference characteristics illustrate  
25 like parts and in which:

Figure 1 is a diagrammatic vertical section taken through the center of the acoustic generator.

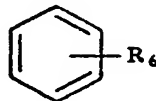
Figure 2 is a diagram showing the vertical cross-section of the acoustic device inserted in a kettle for collecting the initial product and a cyclone separator for separation of the product and recycle of phosgene.

5 In view of the intimate and rapid mixing of the components in the resonance zone, the temperature of the reactants is not as critical as it has been heretofore. Nonetheless, it is desirable and preferred in accordance with the invention that the mist of reactants not exceed an initial temperature of about 100°C. This can be accomplished by employing gaseous phosgene at a temperature within the range of from about 50°C. to about 65°C. to drive  
10 the acoustic device and by keeping the temperature of the organic amines below about 55°C. When preparing aromatic isocyanates from aromatic amines and particularly aromatic polyamines such as toluylene-2,4-diamine, toluylene-2,6-diamine and the like, the initial mixing of the phosgene with the aromatic amine takes place at a temperature so that the resulting mist is below  
15 about 80°C. and then after separating the initial product in a cyclone separator, for example, the initial product is treated with further phosgene in a second step at a high temperature above about 100°C. to convert the initial product into an isocyanate.

20 In accordance with a preferred embodiment of the invention, however, the initial reaction temperature is sufficient so that the amine reacts immediately and fully with the phosgene to prepare the isocyanate which is then removed from the reaction mixture in a second step and need only be purified. Such a process has not been heretofore possible because of inadequate mixing of the amine with phosgene.

25 It is often desirable to prepare a solution of the amine in an inert solvent therefor and inject the solution into the amine nozzle in the resonance zone. Any suitable solvent which is inert to the amine, to the resulting isocyanate and to phosgene may be used.

Thus, suitable solvents are, for example, those which have the formula



wherein R is the same or different and is lower alkyl, hydrogen, halogen, nitro, aryloxy, alkoxy as well as hydrocarbons, ethers, esters and the like. Any suitable lower alkyl group may be used and those which contain from 1 to 4 carbon atoms are preferred such as, for example, methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl as well as alkylene radicals yielding fused ring systems, for example, a butylene radical as in indene and the like. Any suitable halogen may be used such as, for example, chlorine, bromine, iodine, fluorine and the like. Any suitable aryloxy radical may be used such as, for example, phenoxy, cresoxy, ethylphenoxy and the like. Any suitable alkoxy radical may be used such as, for example, ethoxy, methoxy, propoxy, butoxy and the like. Furthermore, mixtures of hydrocarbons such as kerosene may be used. Examples of specific compounds are benzene, toluene, xylene, chlorobenzene, o-dichlorobenzene, tetrahydronaphthylene, 2,4-dichloro-toluene, 4,4'-dichlorodiphenyl, nitrobenzene, cyclohexane, durene, o-, m-, p-cyrenes, dodecyl naphthylene, ethyl acetate, diphenyl and the like.

The invention may be practiced in preparing any aromatic, alicyclic or acyclic monoisocyanate or polyisocyanate from the corresponding amine. Examples of isocyanates which may be prepared include ethyl isocyanate from ethylamine, propyl isocyanate from propylamine, cyclohexyl isocyanate from cyclohexylamine, 2-naphthyl isocyanate from 2-naphthylamine, p-chlorophenyl isocyanate from p-chloroaniline, dichlorohexamethylene diisocyanate from dichlorohexamethyleneamine, hexyl isocyanate from hexylamine, octyl isocyanate from octylamine, dodecyl isocyanate from dodecylamine, octadecyl isocyanate from octadecylamine, tetramethylene diisocyanate from

tetramethylenediamine, pentamethylene diisocyanate from pentamethylene-  
 diamine, hexamethylene diisocyanate from hexamethylenediamine, octa-  
 methylene diisocyanate from octamethylenediamine, undecamethylene diiso-  
 cyanate from undecamethylene diamine, dodecamethylene diisocyanate from  
 5 dodecamethylenediamine, 3,3'-diisocyanato-dipropylether from 3,3'-diamino-  
 dipropylether etc.; cyclohexyl isocyanate from cyclohexylamine, tetrahydro-  
 alpha-naphthyl isocyanate from tetrahydro-alpha-naphthylamine, tetrahydro-  
 beta-naphthyl isocyanate from tetrahydro-beta-naphthylamine, etc.; xylylene  
 diisocyanates from xylylenediamine, diphenylmethane-4,4'-diisocyanate from  
 10 diphenylmethane-4,4'-diamine, beta, beta-diphenylpropane-4,4'-diisocyanate  
 from beta, beta-diphenylpropane-4,4'-diamine, etc.; benzyl isocyanate from  
 benzylamine, phenylethyl isocyanate from phenylethylamine; p-isocyanato  
 benzyl isocyanate from p-aminobenzylamine, etc.; phenyl isocyanate from  
 aniline, o-chlorophenyl isocyanate from o-chloroaniline, m-chlorophenyl iso-  
 15 cyanate from m-chloroaniline, p-ethoxyphenyl isocyanate from p-ethoxy-  
 phenylamine, p-methoxyphenyl isocyanate from p-anisidine, p-cetyl phenyl  
 isocyanate from p-cetylaniline; p-dodecylphenyl isocyanate from p-dodecyl-  
 aniline, 5-dodecyl-2-methylphenyl isocyanate from 5-dodecyl-o-toluidine,  
 3-nitro-4-dodecylphenyl isocyanate from 3-nitro-4-dodecyl aniline; p-cetyl-  
 20 oxyphenyl isocyanate from p-cetyloxyaniline; meta-phenylene diisocyanate  
 from meta-phenylene diamine, p-phenylene diisocyanate from p-phenylene  
 diamine, 2,4-toluylene diisocyanate from 2,4-toluylene diamine, naphthylene-  
 1,4-diisocyanate from naphthylene-1,4-diamine, 2,6-toluylene diisocyanate  
 from 2,6-toluylene diamine, 1,3,5-benzene triisocyanate from 1,3,5-ben-  
 25 zene triamine, 2,4,4'-triisocyanatodiphenylether from 2,4,4'-triaminodi-  
 phenyl ether etc.; tetrahydrofurfuryl isocyanate from tetrahydrofurfuryl-  
 amine, furfurylidene diisocyanate from furfurylidene diamine and the like.

The most convenient apparatus for carrying out the invention is

to attach the acoustic device to the inlet to a continuous centrifugal separator such as a cyclone separator and remove the product immediately from the excess phosgene and then separate any by-product formed by distillation. Often the product is pure enough and satisfactory for sale without any further refining at all other than removal of hydrogen chloride and the highly toxic phosgene. Isocyanates are useful where they have been used heretofore, for example, for the preparation of polyurethane plastics, insecticides and the like. Polyurethanes are in turn useful as cushions, if they are made into cellular products, or as gear wheels, if homogeneous plastics are prepared.

10 The invention is further illustrated by the following examples in which parts are by weight unless otherwise specified.

#### EXAMPLE 1

Phosgene vapor at about 50 lbs/in<sup>2</sup> gauge at about 60°C. is fed at a rate of about 30 to 35 S. C. F. M. through the nozzle 2 of an acoustic generator 1 as shown in Figure 2. A 10% solution in orthene of a mixture of about 80% 2,4- and 20% 2,6-toluylene diamine at about 45°C. is fed through an orifice of the annular chamber 3 about the acoustic generator as shown in Figure 2 at a rate of about 10 lbs. solution per minute. A mist thereby generated in the jacketed water cooled kettle 4 shown in Figure 2 which may have a capacity of 500 gallons i. e. a diameter of about three feet and may be equipped with a bottom nozzle (not shown) for cleaning the kettle. The resulting mist 6 which contains toluylene diisocyanate and excess phosgene and unreacted and partially reacted toluylene diamine is withdrawn from the kettle to a jacketed cyclone separator 5 which is cooled with water to a temperature of about 75°C. The liquid isocyanate reaction mixture is taken from the bottom of the cyclone separator and passed to a tower (not shown) where it is heated to a temperature of about 185°C. for a residence time of about two



hours to insure completion of the reaction. The vapor from the top of the cyclone separator is passed through a demister to a centrifugal compressor and refrigerated condensor to liquify the phosgene and to separate the hydrochloric acid as a gas. The liquid phosgene condensate is supplemented with  
5 additional phosgene to replace that used in the reaction and the combined streams are fed to a vaporizer and thus fed again to the acoustic generator. The nozzle of the acoustic generator in the foregoing example is operated at a frequency of about 10,000 to about 20,000 cycles per second. There are  
10 eight orifices in the radial face of the annular chamber shown in the cross-section in Figure 2 each having a diameter of about 0.04 inches and equally spaced about the lower face of the annular chamber so that they discharge into the high frequency resonating zone of the acoustic generator.

The toluylene diisocyanate produced in accordance with the foregoing example is of exceptionally high purity and when distilled from the reaction mixture in which it was prepared produces very little of the residue  
15 ordinarily obtained in distilling isocyanates from the reaction mixture in which they are prepared. This exceptional purity and high yield is believed to be due to the almost instantaneous and complete mixing of the components in the resonance zone of the acoustic generator.

20

#### EXAMPLE 2

The foregoing example is repeated using the device where the acoustic generator is placed in the inlet to the cyclone separator and the mist from the acoustic generator, is discharged directly into the cyclone separator.

#### EXAMPLE 3

25

Example 1 is repeated except that a solution in monochlorobenzene of 1, 6-hexane diamine is used and fed through the orifice of the annular cham-

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ber at a temperature of about 35°C. The resulting isocyanate is again recovered in good yield and is of exceptionally high purity.

5 Although the invention has been described in considerable detail in the foregoing, it is to be understood that such detail is solely for the purpose of illustration and that many variations can be made by those skilled in the art without departing from the spirit and scope of the invention except as set forth in the claims.

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WHAT IS CLAIMED IS:

1. A method for the production of an organic isocyanate which comprises driving an acoustic generator with phosgene at a frequency in the range of from about 10 kilocycles to about 30 kilocycles to create a resonance zone at said frequency, injecting an organic amine into said resonance zone to intimately mix and react said phosgene with said organic amine and collecting the product from the resonance zone.

2. A method of phosgenating an organic amine which comprises passing phosgene gas at high velocity through an acoustic generator to create a resonance zone at a frequency of from about 10 kilocycles to about 30 kilocycles, injecting an organic amine into said resonance zone to create a mist of reacting organic amine and phosgene, and isocyanate and separating the resulting isocyanate from the excess phosgene.

3. The method of Claim 2 wherein said amine is mixed with an inert solvent and introduced into said resonance zone in a plurality of streams.

4. A method of phosgenating an aromatic diamine which comprises introducing a stream of aromatic diamine in an inert organic solvent therefor into a resonance zone resulting from passing phosgene into an acoustic generator to create a resonance zone at a frequency of from about 10 kilocycles to about 30 kilocycles.

5. A method of mixing phosgene and amines which employs high frequency sonic vibrations to supply the mixing energy.

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6. The method of Claim 1 wherein said organic isocyanate is an organic isocyanate and said organic amine is the corresponding organic polyamine.

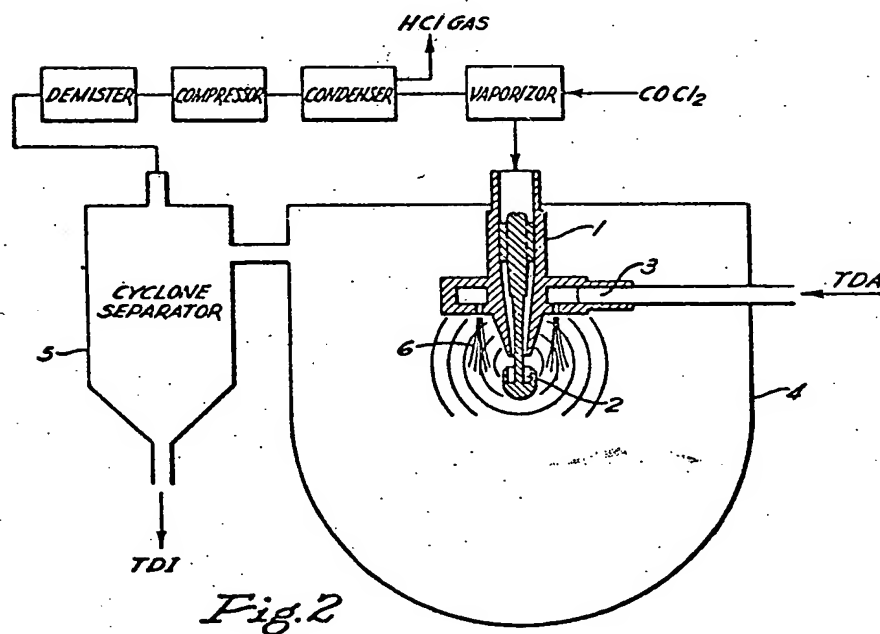
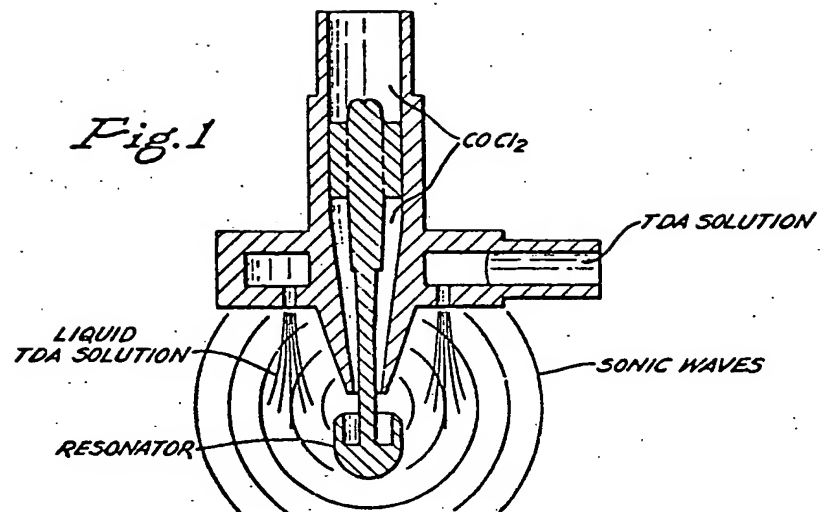
7. The method of Claim 1 wherein said organic amine is a liquid.

8. The method of Claim 4 wherein said aromatic diamine is tolylene diamine.

9. The method of Claim 2 wherein the resulting mixture of reactants does not exceed a temperature of about 100°C.

10. The method of Claim 2 wherein the resulting isocyanate is separated from excess phosgene in a continuous centrifugal separator.





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